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PATENT SPECIFICATION

673.651



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Application Date: Feb. 7, 1949. No. 3356/49.

Complete Specification Published: June 11, 1952.

Index at acceptance:—Classes 2(iii), C1c; and 2(v), RP11a, RP11d(2x: 7), RP11(fx: p6f).

COMPLETE SPECIFICATION

New Polymers

SPECIFICATION NO. 673651

INVENTOR:—MICHAEL MOJZESZ SZWARC

By a direction given under Section 17(1) of the Patents Act 1949 this application proceeded in the name of Petrocarbon Limited, a British company, of 170, Piccadilly, London, W.1.

THE PATENT OFFICE,
10th September, 1952

DB 33432/1(4)/3290 150 9/52 R

temperature between 700 and 1000° C. for not more than 10 seconds and the resulting vapours are cooled to a temperature at which a solid polymer is deposited.

It has now been found that *p*-xylene when substituted additionally in the nuclear structure by one or more atoms of the normally gaseous halogens, i.e. fluorine and chlorine, will also yield a polymer on pyrolysis of the vapour and subsequent cooling.

The invention thus consists in a process for the production of a polymer in which the vapour of *p*-xylene substituted in the nucleus by at least one atom of the normally gaseous halogens is pyrolysed by being subjected to a temperature between 700 and 1000° C. for not more than 10 seconds and the resulting vapours are cooled to a temperature at which a solid polymer is deposited.

Examples of compounds which may be used in the process of the invention for the production of polymers are

2-fluoro-*p*-xylene,
2-chloro-*p*-xylene, and
2,5-dichloro-*p*-xylene.

The pyrolysis step of the process of the invention is preferably carried out by

taneously on condensation of the monomer vapour by cooling. The cooling may take place in contact with a cool surface on which the polymer is deposited in the form of a film.

The temperature to which the monomer vapour formed by pyrolysis should be cooled for condensation and polymerisation to take place can easily be determined by experiment. It depends on the partial vapour pressure of the monomer in the gas phase. The upper limit increases with increasing partial vapour pressure. Generally speaking, the operative temperature range for cooling will be between about 100° C. and -80° C. though higher temperatures may be found effective with high partial vapour pressures of the monomer.

Experiments carried out by reacting the pyrolysed vapours of 2-fluoro-*p*-xylene with iodine vapour have resulted in the production of a compound which is deposited, in addition to the deposition of polymer, in the form of white needles having a melting point of 150–151° C. The results obtained on analysis of this compound indicate that it is 2-fluoro-*p*-xylylene di-iodide, i.e.

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COMPLETE SPECIFICATION

New Polymers

I, MICHAEL MOJZESZ SZWARC, an Israeli citizen, of 33, King's Road, Prestwich, Manchester, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of new and useful polymers.

In earlier Patent Application in Great Britain No. 25562/47 (Serial No. 650,947) there is described a process for the production of a polymer in which the vapour of *p*-xylene is pyrolysed by being subjected to a temperature between 700 and 1000° C. for not more than 10 seconds and the resulting vapours are cooled to a temperature at which a solid polymer is deposited.

It has now been found that *p*-xylene when substituted additionally in the nuclear structure by one or more atoms of the normally gaseous halogens, i.e. fluorine and chlorine, will also yield a polymer on pyrolysis of the vapour and subsequent cooling.

The invention thus consists in a process for the production of a polymer in which the vapour of *p*-xylene substituted in the nucleus by at least one atom of the normally gaseous halogens is pyrolysed by being subjected to a temperature between 700 and 1000° C. for not more than 10 seconds and the resulting vapours are cooled to a temperature at which a solid polymer is deposited.

Examples of compounds which may be used in the process of the invention for the production of polymers are

2-fluoro-*p*-xylene,
2-chloro-*p*-xylene, and
2,5-dichloro-*p*-xylene.

The pyrolysis step of the process of the invention is preferably carried out by

subjecting the vapour of the aromatic compound to a temperature between 700 and 900° C. for from 0.1 to 1 seconds.

Pressures in excess of atmospheric pressure should be avoided in carrying out the process of the invention. Preferably the pressure exerted by the vapour which is subjected to pyrolysis is below atmospheric pressure. The vapour subjected to pyrolysis may be diluted with an inert carrier gas such as nitrogen or carbon dioxide in order to maintain a low partial vapour pressure of the aromatic compound.

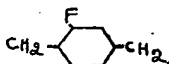
Polymerisation takes place spontaneously on condensation of the monomer vapour by cooling. The cooling may take place in contact with a cool surface on which the polymer is deposited in the form of a film.

The temperature to which the monomer vapour formed by pyrolysis should be cooled for condensation and polymerisation to take place can easily be determined by experiment. It depends on the partial vapour pressure of the monomer in the gas phase. The upper limit increases with increasing partial vapour pressure. Generally speaking, the operative temperature range for cooling will be between about 100° C. and -80° C. though higher temperatures may be found effective with high partial vapour pressures of the monomer.

Experiments carried out by reacting the pyrolysed vapours of 2-fluoro-*p*-xylene with iodine vapour have resulted in the production of a compound which is deposited, in addition to the deposition of polymer, in the form of white needles having a melting point of 150—151° C. The results obtained on analysis of this compound indicate that it is 2-fluoro-*p*-xylylene di-iodide, i.e.



This indicates that the bi-radical



i.e. 2-fluoro-1,4-dimethylene benzene, exists in the vapour phase in the pyrolysed vapours and it appears that this radical is the monomer of the polymer obtained by applying the process of the invention to 2-fluoro-*p*-xylene.

The ratio of carbon to hydrogen to fluorine in the polymer as determined by analysis confirms this view. Similar results were obtained with the corresponding chloro-compound.

Generally stated, the monomers of the polymers produced by the process of the invention consist of the original compound with two CH_2 groups instead of two methyl groups substituted in the para positions of the benzene nucleus.

The invention also consists in the solid polymers produced by the processes referred to above.

The invention thus also consists in a solid polymer, the monomeric unit of which consists of a benzene nucleus with two CH_2 groups substituted in the para positions of the nucleus and substituted additionally in the nucleus by at least one atom of the normally gaseous halogens.

The invention also consists in a solid polymer, the monomeric unit of which is 2-fluoro-1,4-dimethylene benzene or 2-chloro-1,4-dimethylene benzene or 2,5-dichloro-1,4-dimethylene benzene.

Following are the examples of processes for the production of new polymers in accordance with the invention:

EXAMPLE 1.

2-fluoro-*p*-xylene vapour at a pressure of 8 to 10 mm. Hg. abs. was passed through a tube heated to 800°C . at such a rate that the vapour was subjected to this temperature for from 0.3 to 0.4 seconds. The vapours leaving the tube were passed into a trap in which they were cooled to 0°C . in contact with a cold surface on which the polymerised product was deposited in the form of a white occasionally transparent film.

The yield of polymer was approximately 10% by weight of the 2-fluoro-*p*-xylene treated. Unconverted 2-fluoro-*p*-xylene was condensed in another trap cooled to -80°C .

EXAMPLE 2.

2-chloro-*p*-xylene vapour at a pressure of 8 to 10 mm. Hg. absolute was passed through a tube heated to 800°C . at such a rate that the vapour was subjected to this temperature for from 0.3 to 0.4 seconds. The vapours leaving the tube were cooled to room temperature and the polymerised product was deposited.

The polymer was in the form of a film similar to that obtained in example 1.

EXAMPLE 3.

2,5-dichloro-*p*-xylene vapour at a pressure of 8 to 10 mm. Hg. absolute was passed through a tube heated to 800°C . at such a rate that the vapour was subjected to this temperature for from 0.3 to 0.4 seconds. The vapours leaving the tube were cooled to about 50°C . and the polymerised product was deposited.

The polymer was in the form of a film similar to that obtained in example 1.

All the polymers obtained in the above examples had great thermal stability and did not soften when heated up to a temperature of 270°C . They were insoluble in, and also did not swell visibly in, boiling

| | |
|---------------------|----|
| ethyl alcohol | 85 |
| diethylether | |
| chloroform | |
| xylene | |
| benzene | |
| toluene | 90 |
| glacial acetic acid | |

The polymers according to the present invention possess good heat and electrical insulating properties and can be used with advantage for electrical insulation when high temperatures are likely to be encountered. They also have good resistance to corrosive liquids, and can be used as a protection against the effects of such liquids.

What I claim is:—

1. A process for the production of a solid polymer in which the vapour of *p*-xylene substituted in the nucleus by at least one atom of the normally gaseous halogens, is pyrolysed by being subjected to a temperature between 700 and 1000°C . for not more than 10 seconds and the resulting vapours are cooled to a temperature at which a solid polymer is deposited.

2. A process for the production of a solid polymer in which the vapour of 2-fluoro-*p*-xylene is pyrolysed by being subjected to a temperature between 700 and 1000°C . for not more than 10 seconds and the resulting vapours are cooled to a temperature at which a solid polymer is deposited.

3. A process for the production of a solid polymer in which the vapour of 2-chloro-*p*-xylene is pyrolysed by being subjected to a temperature between 700 and 1000° C. for not more than 10 seconds and the resulting vapours are cooled to a temperature at which a solid polymer is deposited.
4. A process for the production of a solid polymer in which the vapour of 2,5-dichloro-*p*-xylene is pyrolysed by being subjected to a temperature between 700 and 1000° C. for not more than 10 seconds and the resulting vapours are cooled to a temperature at which a solid polymer is deposited.
5. A process as claimed in any of the preceding claims in which the pyrolysis is carried out with the vapour of the aromatic compound exerting a pressure below atmospheric pressure.
6. A process as claimed in any of the preceding claims in which the pyrolysis is carried out at a temperature between 700 and 900° C.
7. A process as claimed in any of the preceding claims in which the vapour of the aromatic compound is subjected to the temperature of pyrolysis for from 0.1 to 1 seconds.
8. A process as claimed in any of the preceding claims in which after pyrolysis the resulting vapours are cooled in contact with a cold surface to a temperature at which the polymer is deposited on the said surface in the form of a film.
9. A process as claimed in any of the preceding claims in which the pyrolysis is carried out with the vapour of the aromatic compound diluted with an inert gas.
10. A process as claimed in any of the preceding claims in which the resulting vapours are cooled to a temperature between about 100° C. and -80° C.
11. A solid polymer, the monomeric unit of which consists of a benzene nucleus with two CH₂ groups substituted in the para positions of the nucleus and substituted additionally in the nucleus by at least one atom of the normally gaseous halogens.
12. A solid polymer, the monomeric unit of which is 2-fluoro-1,4-dimethylene benzene.
13. A solid polymer, the monomeric unit of which is 2-chloro-1,4-dimethylene benzene.
14. A solid polymer, the monomeric unit of which is 2,5-dichloro-1,4-dimethylene benzene.
15. A process for the production of a solid polymer substantially as herein-before described.
16. A process for the production of a solid polymer substantially as described in any one of examples 1 to 3.
17. A solid polymer when produced by the process claimed in any of claims 1 to 10 or in claim 15 or 16.

Dated this 2nd day of February, 1950.
N. GAVRON,
Agent for the Applicant.

PROVISIONAL SPECIFICATION

New Polymers

I, MICHAEL MOJZESZ SZWARC, an Israeli citizen, of 33, King's Road, Prestwich, Manchester, do hereby declare the nature of this invention to be as follows:—

My invention relates to the production of new and useful polymers.

In my earlier Patent Application No. 25562/47 I have described a process for the production of a polymer in which the vapour of an aromatic hydrocarbon consisting of from 1 to 4 benzene nuclei with two methyl groups substituted in the para positions of one benzene nucleus and formed only of condensed benzene nuclei when consisting of more than one nucleus, is pyrolysed by being subjected to a temperature between 700 and 1000° C. for not more than 10 seconds and the resulting vapours are cooled to a temperature

at which a solid polymer is deposited.

I have now found that the compounds referred to above when substituted additionally in the nuclear structure by a halogen element or elements will also yield a polymer on pyrolysis of the vapour and subsequent cooling.

Thus, my invention consists in a process for the production of a polymer in which the vapour of an aromatic compound consisting of from one to four benzene nuclei with two methyl groups substituted in the para positions of one benzene nucleus and with one or more halogen atoms substituted in the nucleus or nuclei and formed only of condensed benzene nuclei when consisting of more than one nucleus, is pyrolysed by being subjected to a temperature between 700 and 1000° C. for not more than 10

seconds and the resulting vapours are cooled to a temperature at which a solid polymer is deposited.

Examples of compounds which may be used in the process of the invention for the production of polymers are

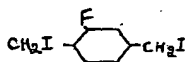
2 fluoro-*p*-xylene and 2 chloro-*p*-xylene.

The pyrolysis step of the process of the invention is preferably carried out by subjecting the vapour of the aromatic hydrocarbon to a temperature between 700 and 900° C. for from 0.1 to 1 seconds.

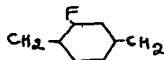
High pressures, e.g. pressures above about 3 atmospheres, should be avoided in carrying out the process of the invention. Preferably the pressure exerted by the vapour which is subjected to pyrolysis is in the region of atmospheric pressure or below. The vapour subjected to pyrolysis may be diluted with an inert carrier gas such as nitrogen or carbon dioxide in order to maintain a low partial vapour pressure of the aromatic hydrocarbon.

Polymerisation takes place spontaneously on condensation of the monomer vapour by cooling. The cooling may take place in contact with a cool surface on which the polymer is deposited in the form of a film.

Experiments carried out by reacting the pyrolysed vapours of 2 fluoro-*p*-xylene with iodine vapour have resulted in the production of a compound which is deposited, in addition to the deposition of polymer, in the form of white needles having a melting point of 150–151° C. The results obtained on analysis of this compound indicate that it is 2 fluoro-*p*-xylylene di-iodide, i.e.



This indicates that the bi-radical



exists in the vapour phase in the pyrolysed vapours and it appears that this radical is the monomer of the polymer obtained by applying the process of the invention to 2 fluoro-*p*-xylene. The ratio of carbon to hydrogen to fluorine in the polymer as determined by analysis confirms this view. Similar results were obtained with the corresponding chloro-compound.

Generally stated, the recurring units

of the polymers produced by the process of the invention thus consist of the original compound with two CH_2 groups instead of two methyl groups substituted in the para positions of one benzene nucleus.

The invention also consists in a process for the production of a polymer by the condensation of the vapour of an aromatic compound consisting of from one to four benzene nuclei with two CH_2 groups substituted in the para positions of one benzene nucleus and with one or more halogen atoms substituted in the nucleus or nuclei, and formed only of condensed benzene nuclei when consisting of more than one nucleus.

The aromatic compound in vapour form which is subjected to condensation to produce a polymer in accordance with the preceding paragraph, may be obtained by the pyrolysis of the vapour of the corresponding dimethyl aromatic compound resulting in the removal of a hydrogen atom from each methyl group.

The invention also consists in the polymers produced by the processes referred to above.

The temperature to which the monomer vapour formed by pyrolysis should be cooled for condensation and polymerisation to take place can easily be determined by experiment. It depends on the partial vapour pressure of the monomer in the gas phase. The upper limit increases with increasing partial vapour pressure. Generally speaking, the operative temperature range for cooling will be between room temperature and -80° C., though higher temperatures may be found effective with high partial vapour pressures of the monomer.

Condensation and simultaneous polymerisation may take place in successive stages at progressively reduced temperatures, that is the vapours leaving the first condensation and polymerisation stage are further cooled to condense and polymerise a further portion of the residual monomer vapour and so on.

Following are examples of processes for the production of new polymers in accordance with the invention:

EXAMPLE I.

2 fluoro-*p*-xylene vapour at a pressure of 8 to 10 mm. Hg. was passed through a tube heated to about 800° C. at such a rate that the vapour was subjected to this temperature for from 0.3 to 0.4 seconds. The vapours leaving the tube were passed into a trap in which they were cooled to 0° C. in contact with a cold surface on which the polymerised

product was deposited in the form of a white occasionally transparent film.

The yield of polymer was approximately 10% by weight of the 2 fluoro-*p*-xylene treated. Unconverted 2 fluoro-*p*-xylene was condensed in another trap cooled to -80°C .

EXAMPLE 2.

2 chloro-*p*-xylene vapour at a pressure of about 10 mm. Hg. was passed through a tube heated to about 300°C . at such a rate that the vapour was subjected to this temperature for about 0.4 seconds. The vapours leaving the tube were cooled to room temperature and the polymerised product was deposited.

The polymer was in the form of a film similar to that obtained in example 1.

All the polymers obtained in the above examples had great thermal stability and did not soften when heated up to a temperature of 270°C . They were not attacked by sulphuric acid at 150°C . They were insoluble in, and also did not swell visibly in, boiling

ethyl alcohol
diethylether
chloroform
xylenes
benzene
toluene
glacial acetic acid.

25

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Dated this 7th day of February, 1949.

N. GAVRON,

Agent for the Applicant.